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(54) **Method for preparing silyl-terminated polyolefins**

(57) Disclosed herein is a method for synthesizing polyolefins having a silyl group at one terminus, said

method comprising polymerizing α -olefins in the presence of a metallocene catalyst using silane as a chain transfer agent.

EP 0 739 910 A2

Description

The present invention relates to a method for the preparation of silyl-functionalized polyolefins. More particularly, the invention introduces a method for synthesizing polyolefins having a silyl group at one terminus, said method comprising polymerizing α -olefins in the presence of a metallocene catalyst using silane as a chain transfer agent.

The production of polyethylene and copolymers of polyethylene with α -olefins by Ziegler-Natta polymerization processes has evolved considerably since their introduction in the early 1950s. Control of molecular weight (MW) is important as it influences the final physical properties of the polymer. The MW is controlled by chain transfer reactions which terminate the growth of the polymer chains. A number of such chain transfer processes, including β -H elimination, β -alkyl elimination, and chain transfer to MR_2 ($M = Zn, Al$, etc.), monomer and hydrogen have been identified. Of these, hydrogen is the only practical chain transfer agent since it is easy to use and does not affect the activity of the catalyst. However, there are many cases where even hydrogen does not provide the optimum results due to undesired side effects (e.g., unresponsive M-R bonds, over activation of the catalyst or too rapid hydrogenation of other functional groups). Therefore, alternative chain transfer agents for use in the production of polyethylene, and copolymers thereof, are highly desirable.

Furthermore, the use of hydrogen as a chain transfer agent results in a non-functional, saturated polymer chain end, whereas terminally functionalized polymer is of great current interest. Such a polymer has use as precursor for making block or graft polymers and is expected to exhibit modified chemical and physical properties. A silyl-functional polyethylene of this type has been prepared by Brookhart et al. (*Polymer Preprints, Vol. 35(1), 1994*) using a cationic cobalt alkyl complex. However, this synthesis presents the following disadvantages: 1) this process is not truly catalytic; 2) the silane does not act as a chain transfer agent and therefore does not control molecular weight of the target polymer; 3) the silane does not regenerate a catalyst; and 4) the method is only effective with ethylene while substituted olefins, such as propylene and butylene, do not react when using cobalt initiator.

It has also been disclosed in United States Patent 4,965,386 that an olefin can be hydrosilated by contacting the α -olefin with a silane in the presence of a metallocene catalyst. In this preparation, only the silylated monomeric product was obtained. The patentee does not suggest the formation of a polymer or any hydrosilated product derived from repetitive olefin insertion, nor do they suggest the use of ethylene or mixtures of ethylene and an α -olefin.

Surprisingly, we have found that certain silanes can be used as chain transfer agents when ethylene, or a combination of ethylene and an α -olefin, is polymerized with certain metallocene catalysts. Unlike the procedures cited above, the instant method results in an ethylene polymer, or interpolmer of ethylene and an α -olefin, having a silyl group at one terminus of its chain. Moreover, the method of the present invention is catalytic and has a significantly improved rate of polymer production relative to the preparation described by Brookhart et al., cited above, and is therefore more suitable for commercial application.

The method of the present invention, therefore, comprises reacting (A) ethylene, or a combination of ethylene and an α -olefin, and (B) a silane in the presence of (C) a catalyst comprising a metallocene compound to form the corresponding polyethylene homopolymer or interpolmer of ethylene and α -olefin, having one silyl terminal group.

Component (A) of this invention is selected from ethylene or a combination of ethylene and at least one α -olefin having the general formula $H_2C=CH(R)$ (i) in which R is a monovalent group selected from alkyl radical having 1 to 10 carbon atoms or an aryl group. Specific examples of suitable α -olefins of formula (i) include styrene, propene, 1-butene, 1-pentene, 1-hexene and 1-octene. Preferably component (A) is ethylene or a combination of ethylene with styrene, propene or 1-hexene. When one or more of the above described α -olefins (i) is used together with ethylene, the resulting product is the corresponding copolymer or terpolymer (i.e., an interpolmer in the general case where at least one comonomer is used). In the present invention, up to 90 mole percent of the α -olefin (i) may be used in component (A). Since the reactivity of the α -olefins is generally less than that of ethylene, a large excess of (i) may be needed to incorporate such olefin units into the interpolmer and such reactivity ratios may be determined by routine experimentation. When component (A) is a combination of ethylene and an α -olefin (i), it is preferred that 10 to 80 mole percent of (i) is used.

Component (B) of the instant method is a silane having the formula $R^2R^3R^4SiH$ (ii) wherein R^2 , R^3 and R^4 each represents a monovalent group independently selected from hydrogen atom, alkyl radicals having 1 to 4 carbon atoms, aryl radicals such as phenyl and tolyl, alkylaryl radicals such as ethylphenyl and ethyltolyl, arylalkyl radicals such as phenylethyl and benzyl, alkoxy radicals having 1 to 4 carbon atoms, phenoxy radical, fluorinated alkyl radicals having 3 to 6 carbon atoms such as 3,3,3-trifluoropropyl, a dialkylamino group in which the alkyl groups contain 1 to 4 carbon atoms and a diorganopolysiloxane chain containing 1 to 10 siloxane units in which the organic groups are independently selected from alkyl radicals having 1 to 4 carbon atoms, aryl radicals, fluorinated alkyl radicals or alkoxy radicals having 1 to 4 carbon atoms.

Preferred groups which are bonded to the silicon atom of formula (ii) include hydrogen, methyl, ethyl, isopropyl, isobutyl, phenyl, methoxy, ethoxy, chlorine, 3,3,3-trifluoropropyl, dimethylamino and siloxane groups of the formula $R'_3SiO(SiR'_2O)_n$ (iv) in which R' is independently selected from methyl, phenyl, 3,3,3-trifluoropropyl, methoxy or ethoxy

groups and j has a value of 0 to 10. Highly preferred silanes of the instant method are phenylsilane, diphenylsilane, phenylmethylsilane, pentamethyldisiloxane, methylsilane and dimethylsilane.

Catalyst (C) is selected from a metallocene catalyst or a metallocene catalyst in combination with a co-catalyst. The metallocene catalyst of our invention has its general formula selected from



or

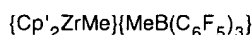
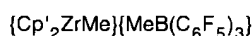
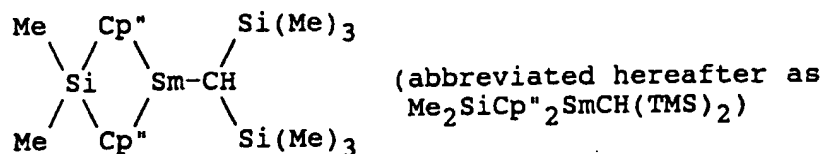
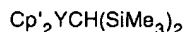
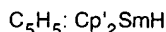


wherein Cp denotes a cyclopentadienyl or a substituted cyclopentadienyl radical. Examples of substituted Cp groups include C_5R^*_5 (applicable to structures vi and vii) and C_5R^*_4 (applicable to structures v and viii), in which R^* is selected from the group consisting of hydrogen atom, alkyl having 1 to 20 carbon atoms, aryl having 6 to 18 carbon atoms and triorganosilyl, such as trimethylsilyl. Specific Cp groups are pentamethylpentadienyl ($\text{Cp}' = \text{h}^5\text{-C}_5\text{Me}_5$) and tetramethylpentadienyl ($\text{Cp}'' = \text{h}^5\text{-C}_5\text{Me}_4$), wherein Me denotes a methyl radical and h^5 indicates pentavalent coordination with the metal, described infra. In formulas (v) through (viii), Z is selected from Si, C, Ge or Sn and R^5 is independently selected from alkyl radicals having 1 to 4 carbon atoms, aryl radicals having 6 to 8 carbon atoms and methoxy. Preferably, Z is Si and each R^5 is methyl. M is a metal selected from the periodic chart as Group 3 elements, Group 4 elements or Lanthanide series elements.

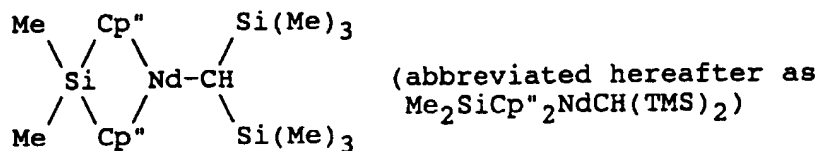
Specifically, M may be Sc, Y, La, Ac, Ti, Zr, Hf, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu.

Preferably M is selected from La, Y, Sm, Zr, Ti, Hf, Nd or Lu. X is a metal ligand selected from hydrogen atom, halogen, alkyl radicals having 1 to 8 carbon atoms, substituted alkyl radicals having 1 to 8 carbon atoms, allylic radicals having 3 to 6 carbon atoms or aryl radicals having 6 to 8 carbon atoms. Q in formulas (vi) and (viii) is an anionic counterion of an element selected from boron, aluminum, gallium, zinc or cadmium. Examples of preferred Q groups include $\{\text{MeB}(\text{C}_6\text{F}_5)_3\}^-$ and $\{\text{B}(\text{C}_6\text{F}_5)_4\}^-$. In these formulas, n and m are integers, each having a value of 1 to 3 such that (m + n) satisfies the valence of metal M.

Specific examples of the above metallocene catalysts include compounds having the following formulas, in which Me, Cp' and Cp'' have their previously defined meanings and Cp''' denotes



and



wherein TMS represents a trimethylsilyl group. Those skilled in the art will, of course, recognize that catalysts such as $Me_2SiCp''_2SmCH(TMS)_2$ undergo a rate-determining activation reaction to form the corresponding hydride (e.g., $Me_2SiCp''_2SmH$).

The above described catalysts are known in the art and are employed in particulate form, as a homogeneous solution or supported on inert materials such as alumina, methylalumoxane-activated silica, silica, silica-alumina and magnesium chloride. They are prepared by methods taught in *Organometallics*, vol. 5, 1726-33, 1986; Möhring et al., *Journal of Organometallic Chemistry*, v. 479, 1-29, 1994, United States Patents 4,871,705, 5,001,205, 4,801,666 or 4,668,773; and *Journal of the American Chemical Society*, v. 107, 8091-8103, 1985.

In the present invention, a co-catalyst is also added when $m = 0$ and $n = 2$ in formulas (v) through (viii) (i.e., when $M = Ti, Zr$ or Hf). This co-catalyst is used, for example, to activate the metallocene catalyst and is selected from alkylalumoxanes, trialkyl boron compounds in which the alkyl radicals have 1 to 8 carbon atoms or triaryl boron compounds in which the aryl radicals have 6 to 8 carbon atoms. A highly preferred co-catalyst is methylalumoxane (MAO). Certain co-catalysts, such as MAO, also act as oxygen scavengers and desiccants and are beneficial for these functions as well. Alternatively, the co-catalyst can be a compound having the formula

$AlG_kR^6_{(3-k)}$ in which G is selected from hydrogen atom, halogen atom, alkyl radicals having 1-8 carbon atoms or aryl radicals having 6 to 8 carbon atoms, R^6 is an alkyl radical having 1-8 carbon atoms and k is an integer having a value of 0 to 3.

Various metallocene catalysts which require a co-catalyst are illustrated in United States Patents 4,871,705 and 5,001,205. Particularly, catalysts having the above formulas (v) through (viii), wherein X = halogen atom, will require a co-catalyst, and MAO is preferably used in combination therewith. Such catalyst combinations are illustrated by the

following, wherein Cp' and Cp have their previously defined meanings (see, e.g., Tritto et al., *Macromolecules*, v. 26, 7111-15, 1993):



and



Based on the instant disclosure or the patent and scientific literature in general, those skilled in the art will readily identify circumstances wherein a co-catalyst is desirable by routine experimentation (e.g., based on rate of reaction, polymer yield and molecular weight).

In a preferred embodiment of the instant method, catalyst (C) and silane (B) are first mixed, preferably in a non-polar hydrocarbon solvent, such as toluene, butane, pentane, hexane, octane and iso-octane. Preferably, the solvent is toluene. Alternatively, the silane itself can act as a solvent if a low molecular weight polymer is desired. The above mixing operation must avoid the introduction of moisture or oxygen. The latter condition may be satisfied by running the reaction under an inert atmosphere, such as nitrogen or argon, as is standard in the art.

Ethylene (or a mixture of ethylene and α -olefin) is introduced while the ingredients are vigorously agitated and the polymerization reaction is carried out at a temperature of -100°C . to 200°C ., preferably at 25 to 80°C . The pressure during polymerization is typically controlled at 0.1 to 10.1 MPa (1 to 100 atmospheres), preferably 1 to 5 atmospheres, and is determined by temperature in a closed system or by the pressure of the volatile components in a continuous polymerization. When an α -olefin having a boiling point above the reaction conditions is used, it may be added simultaneously with the ethylene. When the silane is a gas under the reaction conditions, it may also be added simultaneously with the ethylene (or ethylene plus α -olefin) in the desired ratio to produce the silyl-terminated polymer or interpolymer. Upon completion of the reaction, silyl-terminated polymer generally precipitates out of solution when a solvent is used. The polymer can also be recovered by evaporating the solvent. If the reaction is to be carried out without the use of a solvent (e.g., in a gas phase reaction using a supported catalyst), the reaction temperature is preferably adjusted such that the silane and α -olefin are both gases. In this case, the mixture of ethylene, silane and α -olefin is exposed to the catalyst and the polymer formed is removed as a melt from the bottom of the reactor. The polymer or copolymer may be purified by re-precipitation or by other conventional techniques.

The above polymerization may be summarized by the following generalized equation for ethylene:



wherein R^2 through R^4 are previously defined and x represents the average degree of polymerization (DP). Although we are not bound by a particular mechanism or theory, it is believed that, at least for the lanthanide catalysts of this invention, the metal hydride undergoes rapid multiple ethylene insertion during propagation. This is then followed by polymer chain transfer to the silicon of the silane, resulting in the silyl-capped polyethylene (or ethylene interpolymer when an α -olefin is used), and the simultaneous regeneration of active catalyst, which will readily participate in the next catalytic cycle.

Our invention clearly establishes that silane (B) can serve as an effective chain transfer agent in the polymerization of ethylene, or ethylene in combination with α -olefins, using metallocene catalyst (C). Therefore, the molecular weight of the resulting ethylene polymer or copolymer is controlled by adding the appropriate amount of silane (B), as illustrated infra.

Furthermore, the instant method may be used to prepare a novel silyl-terminated interpolymer between ethylene and at least one of the above described α -olefins wherein one terminus of the interpolymer is a silyl group of the formula $\text{R}^2\text{R}^3\text{R}^4\text{Si}-$ in which R^2 , R^3 and R^4 are defined as above.

We have also found that the rate of information of the silyl-terminated polymer is significantly higher in our process than that observed by Brookhart et al. This rate can be further augmented by increasing the concentration of the α -

olefin (e.g., increased pressure of α -olefin when the latter is a gas), increasing the catalyst concentration or raising the temperature.

The silyl-terminated polyethylene polymer or interpolymer produced by the present invention will find utility in the preparation of block copolymers or star block copolymers (e.g., when the silyl end group contains one or more reactive sites such as SiH) for application as polymer compatibilizers. They may also be used to modify the surface of plastics such as polyolefins for coating or adhesion purposes.

The following examples are presented to further illustrate the method of this invention, but are not to be construed as limiting the invention, which is delineated in the appended claims. All parts and percentages in the examples are on a weight basis and all measurements were obtained at 25°C., unless indicated to the contrary. The notation Ph is used to denote phenyl radical.

Examples 1 - 9

The following procedure was used for the polymerization of ethylene. A dried 25 mL flask equipped with a magnetic bar was charged (in a glove box) with 0.029 mmol of a given catalyst (second column of Table 1). The flask was sealed, removed from the glove box and connected to a high vacuum line, whereupon 10 mL of dry toluene and a measured amount of phenylsilane were condensed into the flask under vacuum at -78°C. The third column of Table 1 shows the molar concentration of silane in toluene used in each case. The mixture was then vigorously stirred and quickly warmed to 23°C. while ethylene gas at 0.1 MPa (1 atmosphere) pressure was introduced to the flask. After a measured time (fourth column of Table 1), the reaction was stopped by the addition of a small amount of methanol. The precipitated polymer was collected by filtration, washed with toluene and acetone, dried under high vacuum, and weighed for yield determination (fifth column of Table 1). Herein the conventional notation of M_n and M_w for number average and weight average molecular weight, respectively, is used.

The ^1H NMR (nuclear magnetic resonance) of each polymer at 140°C. in $\text{C}_2\text{D}_2\text{Cl}_4$ revealed the expected resonance at δ 4.35 ppm that is characteristic of silane protons, which was resolved into a triplet due to the coupling to adjacent CH_2 group ($J = 3.6$ Hz) when the polymer molecular weight was low (M_n : 600-1000). A strong peak at δ 1.32 ppm is attributed to the polyethylene protons. The corresponding ^{13}C NMR signal of the CH_2 group connected to the silyl group was found at δ 11.28 ppm. This split into a triplet ($J = 118$ Hz) in the ^{13}C (^1H coupled) NMR spectrum and the methyl group of the other end of polymer chain had a chemical shift of δ 15.06 ppm ($q, ^1\text{C-H} = 127$ Hz). The presence of the silyl end group was also verified by its strong infrared adsorption at 2109 cm^{-1} , which is typical of Si-H stretching frequency, in addition to the absorptions derived from polyethylene moiety. The absence of resonances at δ 4.5 to 6.0 ppm in the ^1H NMR spectrum indicates that silyl-capped polyethylene was cleanly formed. It is thus believed that β -H elimination, which is responsible for chain termination in the absence of silane is not operative and the process involving chain transfer directly to silicon of the silane reagent (Si-H/M-C transposition) is dominant in our claimed invention.

The catalyst activity was calculated and appears in the sixth column of Table 1, the units being kg of polymer formed per mole of metal per hour. Number average molecular weight and the polydispersity of these silyl-terminated polyethylenes are also shown in the last two columns of Table 1, respectively.

From Table 1 it is seen that, for a given catalyst, increasing the PhSiH_3 concentration resulted in the gradual decrease of the polymer molecular weight (Examples 1-5). When these data were plotted, an essentially linear inverse correlation between M_n and silane concentration was observed, clearly indicating that PhSiH_3 acts as a true chain transfer reagent. The molecular weight distribution of approximately 2 is also consistent with a homogeneous system having identical active centers with one major chain termination. Furthermore, variation of the lanthanide element and ligation of the catalyst show no apparent influence on the molecular weight of the ensuing polymer (Table 1, Examples 4, 6, 7, 8, 9). However, activity increased when the catalyst was sterically relatively open, as shown in Table 1 (La: 828 > Sm: 342 > Y: 300 > Lu: 244 kg/mol of Ln-hour).

It was also observed that the Cp^*_2LuH catalyst (Example 6) resulted in polyethylene having 32 mole percent of vinyl terminal groups (i.e., 32% of the non-methyl ends). It is believed that the vinyl formation in this case, wherein the lanthanide element was relatively small, indicates that the rates of the two competing termination processes of β -H elimination and hydrosilylation are comparable.

TABLE 1. ETHYLENE POLYMERIZATION IN THE PRESENCE OF PhSiH_3 USING ORGANOLANTHANIDE
(Ln) COMPLEXES AS CATALYSTS

Example	Catalyst	(PhSiH_3) (M)	Reaction Time (min)	Yield (g)	Activity (kg/mol of Ln h)	M_n	M_w/M_n
1	$\text{Cp}'_2\text{SmH}$	0.08	2	0.69	713	57000	2.1
2	$\text{Cp}'_2\text{SmH}$	0.24	2	0.80	827	7600	4.2
3	$\text{Cp}'_2\text{SmH}$	0.46	4	0.65	330	5000	6.1
4	$\text{Cp}'_2\text{SmH}$	0.74	2	0.33	342	4400	4.3
5	$\text{Cp}'_2\text{SmH}$	1.06	4	0.64	311	2600	2.8
6	$\text{Cp}'_2\text{LuH}$	0.74	40	4.45	244	2090	5.2
7	$\text{Cp}'_2\text{YH}$	0.74	2	0.35	300	4900	2.2
8	$\text{Cp}'_2\text{LaH}$	0.74	1.5	0.59	828	4090	3.5
9	$\text{Me}_2\text{SiCp}''_2\text{SmCH}(\text{TMS})_2$	0.74	25	0.24	28	2550	2.9

Example 10

The procedure according to Examples 1-9 was repeated wherein 15 mg (0.020 mmol) of $\{Cp^*ZrMe\}\{MeB(C_6F_5)_3\}$ ($Cp^* = C_5H_5^-$), 10 mL of toluene and 2 mL (0.011 mmol) of diphenylsilane (Ph_2SiH_2) were mixed and ethylene at 25.3 kPa (0.25 atmosphere) was introduced at room temperature over a period of one hour. The reaction was stopped by adding 1 mL of methanol and the polymer recovered as before (yield = 1.2 g).

The number average molecular weight of this silyl-terminated polyethylene was 8200. 1H NMR (toluene- d_6 , relative intensity): δ 7.50 (Ph, 0.2), 7.12 (Ph, 0.2); 4.50 (SiH_2 , 0.2); 1.34 $\{(CH_2CH_2)_p, 100\}$.

Examples 11 - 14

The procedure of Example 10 was repeated wherein 14 mg of $\{Cp^*ZrMe\}\{MeB(C_6F_5)_3\}$, 10 mL of toluene and the indicated amount of phenylmethylsilane ($PhMeSiH_2$) shown in the second column of Table 2 (M = molarity in the toluene solution) were mixed and ethylene at 0.1 MPa (1 atmosphere) was introduced at 23°C over a period of 1 hour. The reaction was stopped by adding methanol and the polymers were recovered as before. These reactions are summarized in Table 2.

Table 2

Example	Silane (M)	Time (min)	Yield (g)	M_n	M_w/M_n
11	0.35	5	1.2	3080	6.5
12	0.66	5	1.9	1900	3.6
13	1.68	5	3.3	1280	3.1
14	2.43	15	3.3	1320	4.1

Example 15

The procedure of Examples 1-9 was repeated wherein 15 mg (0.025 mmol) of $Me_2SiCp^*SmCH(TMS)_2$, defined supra, 10 mL of toluene and 1 mL (8.12 mmol) of phenylsilane ($PhSiH_3$) were mixed and ethylene at 25.3 kPa (0.25 atmosphere) was introduced at room temperature over a period of one hour. The reaction was stopped by adding 1 mL of methanol and the polymer recovered as before (yield = 0.52 g).

The number average molecular weight of this silyl-terminated polyethylene was 800. 1H NMR (toluene- d_6 , relative intensity): δ 7.50 (Ph, 1.8), 7.20 (Ph, 2.0); 4.45 (SiH_2 , 1.7); 1.30 $\{(CH_2CH_2)_p, 100\}$.

Example 16

The procedure of Example 15 was repeated wherein 12 mg (0.020 mmol) of $Me_2SiCp^*SmCH(TMS)_2$, defined supra, 10 mL of toluene and 0.5 mL (4.1 mmol) of phenylsilane ($PhSiH_3$) were mixed and 2 mL (16 mmol) of 1-hexene were condensed into the flask at -78°C. The mixture was warmed to 23°C, and ethylene at 0.1 MPa (1 atmosphere) was introduced with vigorous stirring over a period of 3 hours. The reaction was then stopped by adding approximately 1 mL of methanol and the polymer recovered, washed with methanol and acetone and dried as before (yield = 0.5 g).

The number average molecular weight was 1500. 1H NMR ($C_2D_2Cl_4$, 120°C): δ 7.57 (m), 4.35 (t, $J=3.6$ Hz), 1.54 (m), 1.32 (m, strong), 1.15 (m), 0.95 (m, strong). Also from 1H NMR, it was determined that 15% mol of the 1-hexene units were incorporated into this silyl-terminated copolymer.

The above procedure was repeated using between 0.5 and 5.0 mL of 1-hexene dissolved in 10 mL of toluene to prepare silyl-terminated copolymers having a ratio of ethylene to hexene units in the range of 10:1 to 10:6, respectively. As before, NMR analysis (1H , ^{13}C) of the polymer revealed the expected silane resonances.

Example 17

In a glove box, a 25 mL flamed, round-bottom flask equipped with a magnetic stirrer, was charged with 18 mg (0.031 mmol) of a catalyst having the formula $Me_2SiCp^*NdCH(TMS)_2$, wherein Cp* and TMS are as defined supra, and 1.04 g (10 mol) of styrene. The flask was connected to a high vacuum line and 10 mL of toluene and 0.2 mL (0.18 g, 1.62 mmol) of phenylsilane were condensed in under vacuum at -78°C. The mixture was then exposed to ethylene at 0.1 MPa (1 atmosphere) and vigorously stirred for 20 hours at 23°C. The reaction was stopped by the addition of methanol and the volatiles were evaporated off in vacuo. The resulting polymer was washed with methanol and acetone and dried under high vacuum to provide a yield

of 1.70 g.

Polymer composition: 26% styrene incorporation in the polymer based on ^1H NMR analysis; $M_n = 3300$.

^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110°C): δ 7.70-6.95 (m, Ph, strong), 4.35 (m, PhH_2Si -), 2.80-2.30 (m, $-\text{CH}(\text{Ph})-$), 1.70-1.40 (m, CH_2CHPh -, strong), 1.40-0.90 (m, CH_2CH_2 -, very strong).

^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110°C): δ 146.61, 135.67, 135.63, 135.19, 129.70, 129.59, 129.42, 128.37, 128.32, 128.21, 128.09, 127.94, 127.85, 127.78, 127.67, 127.19, 127.09, 126.95, 125.57, 125.00, 46.05, 45.75, 36.83, 36.75, 36.65, 29.62, 29.60, 29.468, 29.32, 27.55, 27.37, 25.42, 22.02, 16.61.

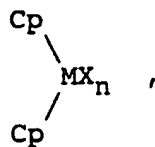
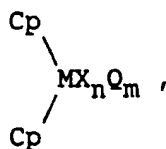
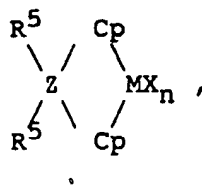
Claims

1. A process for preparing a silyl-terminated polyethylene comprising reacting

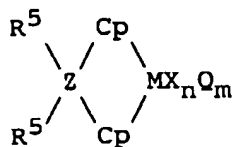
(A) at least one monomer selected from ethylene or a combination of ethylene and an α -olefin having the formula $\text{H}_2\text{C}=\text{CH}(\text{R})$, in which R represents a monovalent group selected from alkyl radical having 1 to 10 carbon atoms or aryl radical; and

(B) a silane having the formula $\text{R}^2\text{R}^3\text{R}^4\text{SiH}$ wherein R^2 , R^3 and R^4 each represents a monovalent group independently selected from the group consisting of hydrogen atom, alkyl radicals having 1 to 4 carbon atoms, aryl radicals, alkylaryl radicals, arylalkyl radicals, alkoxy radicals having 1-4 carbon atoms, phenoxy radical, fluorinated alkyl radicals having 3 to 6 carbon atoms, dialkylamino group in which the alkyl groups contain 1 to 4 carbon atoms and a diorganopolysiloxane chain containing 1 to 10 siloxane units, said reaction taking place in the presence of

(C) a catalyst comprising a metallocene compound having its formula selected from the group consisting of



and



wherein Cp denotes a cyclopentadienyl or a substituted cyclopentadienyl radical, Z is selected from the group consisting of Si, C, Ge and Sn, R⁵ is selected from the group consisting of alkyl radicals having 1 to 4 carbon atoms, aryl radicals and methoxy, M is a metal selected from the group of the periodic table consisting of Group 3 elements, Group 4 elements and Lanthanide series elements, X is a metal ligand selected from the group consisting of hydrogen atom, halogen atom, alkyl radicals having 1 to 8 carbon atoms, substituted alkyl radicals having 1 to 8 carbon atoms, allylic radicals having 3 to 6 carbon atoms and aryl radicals having 6 to 8 carbon atoms, Q is an anionic counterion of an element selected from the group consisting of boron, aluminum, gallium, zinc and cadmium and n and m are integers, each having a value of 1 to 3 such that (m + n) is selected to satisfy the valence of said metal M.

2. The process of claim 1 wherein catalyst (C) consists of a combination of said metallocene compound and a co-catalyst selected from the group consisting of an alkylalumoxane, a trialkyl boron compound in which the alkyl radicals have 1 to 8 carbon atoms, a triaryl boron compound having 6 to 8 carbon atoms and a compound of the formula $AlG_kR^6_{(3-k)}$ in which G is selected from the group consisting of hydrogen atom, halogen atom, alkyl radicals having 1-8 carbon atoms, aryl radicals having 6 to 8 carbon atoms, R⁶ is an alkyl radical having 1-8 carbon atoms and k is an integer having a value of 0 to 3.
3. The process according to claim 1 wherein component (A) is a combination of ethylene and a compound selected from the group consisting of styrene, propene and 1-hexene.
4. The process according to any of claims 1-3 wherein said silane (B) is selected from the group consisting of phenylsilane, diphenylsilane, phenylmethylsilane, pentamethyldisiloxane, methylsilane and dimethylsilane.
5. The polymer obtainable by the method of any of claims 1-4.